

Symposium on Advances in Fischer-Tropsch Chemistry
Presented Before the Division of Petroleum Chemistry, Inc.
219th National Meeting, American Chemical Society
San Francisco, CA, March 26-31, 2000

CO Hydrogenation over Co/SiO₂ Catalysts Prepared by Different Ways

Claudia L. Bianchi, Federica Martini and Vittorio Ragani
Dept. Physical Chemistry and Electrochemistry
University of Milano
Via Golgi, 19
20133 Milano, Italy

Pietro Moggi
Dept. Organic and Industrial Chemistry
University of Parma
Parco Area delle Scienze, 17/A
43100 Parma, Italy

INTRODUCTION

Cobalt-based catalysts are highly investigated for Fischer-Tropsch synthesis: they are highly active, selective for linear hydrocarbons, scarcely active for the competing water-gas shift reaction; their price is quite low, compared to noble metals (1).

Many authors have already studied the role of support. At atmospheric pressure and at low conversion, Reuel and Bartolomew (2) reported, with 10 wt% Co supported catalysts, an increase in specific activity (at $P = 0.1$ MPa, $T = 498$ K, $H_2/CO = 2$) depending on the nature of the support in the following order: $Co/MgO < Co/C < Co/SiO_2 < Co/Al_2O_3 < Co/TiO_2$. However, the works of Iglesia et al. (3) at higher pressure ($P > 0.5$ MPa) and at high conversion, indicate that the influence of the support on the specific activity and the methane and C₅ hydrocarbons selectivity can be neglected. According to these authors (3) the reaction is insensitive to the structure of cobalt respectively its dispersion.

However, the chemical nature of the support, its surface-acid-base properties and its texture play a very important role. For an acid support it was reported that the long residence time would favor the hydrogenolysis and hence the production of lighter products (4). Besides, the pore size and the acid properties can influence the metal support interaction and lead to the formation of well defined phases as cobalt silicate, aluminate or lanthanate.

Moreover, the nature of the cobalt precursor has a large influence on the reducibility of cobalt and on its activity and selectivity. Niemela et al. (5) reported the following order in activity for 5% Co/SiO₂: $Co_2CO_8 > Co(NO_3)_2 > Co(CH_3COO)_2$, but Co-

bolt(II) nitrate seems to be the best precursor for high activity and long chain hydrocarbon formation.

In the present work, an extensive study of different preparation methods for Co/SiO₂ catalysts is reported. In addition to the conventional impregnation, other more innovative methods are tested together with the sol-gel process which is now largely used especially for the synthesis of silica gel (6, 7). This process would allow to master the specific surface area, the porosity and particle size of the sample (8, 9).

All the prepared samples have been fully characterized and tested in a bench scale fixed bed reactor.

EXPERIMENTAL

Sample Preparation

Five different preparation methods were used in this paper. All the catalysts were prepared using the same kind of silica (by Aldrich, surface area 520 m²/g) and the same precursor: cobalt nitrate hexahydrate (Fluka).

The first method was the classical incipient wetness impregnation (sample named CS, "classical sample"). The support was impregnated with an aqueous solution of cobalt nitrate hexahydrate in a single step followed by a calcination-reduction in pure flowing hydrogen (99.99% purity grade), at 375°C for 16 hr (flow rate = 50 ml H₂/min). The reduction schedule included a temperature ramp of 3°C/min (from room temperature) with half-hour holds at 100°C to facilitate water removal and

at 200°C to ensure controlled nitrate decomposition.

The second method was the ammonia one as described by Barbier et al. (10) (sample named AS "ammonia sample"). The precursor was added to a suitable amount of water at room temperature and stirred by a magnetic rod; to prevent Co^{2+} oxidation dissolved oxygen was removed by boiling the water and the system was protected from air by an argon blanket. A solution of ammonia was poured in the solution bringing about the precipitation of $\text{Co}(\text{OH})_2$ (this precipitate is dissolved by a large excess of ammonia). The support was then added to the solution and its pH reached an equilibrium value near 12.0 after stirring 1 h. After equilibrium, the system was stirred for one additional hour, then centrifuged and washed five times. Finally it was dried in a vacuum oven at 80°C overnight and reduced into flowing hydrogen following the steps described for sample CS.

Ultrasound (US) was used for the third and fourth preparation methods to improve the metal dispersion (11, 12).

In the third preparation (sample named CRUS "classical reduced with US sample"), the impregnation was performed as for CS, but before reducing the catalyst in flowing hydrogen, the sample was added to a solution of pure hydrazine at 80°C and here left under sonication (20 kHz) for 15 min as described in (12).

In the fourth method (sample named USS "Ultrasound sample") the aqueous solution of cobalt nitrate was directly added to the silica under sonication (20 kHz) for 1 h at room temperature and then reduced in flowing hydrogen following the steps described for CS.

Sample 5 (named SGS "sol-gel sample") was prepared via sol-gel

Table 1.
Characterization Data

Sample	Co wt.-%	Surface area (m^2/g)	Metal dispersion D_{Co} (%)
SiO_2	—	520	—
CS	5	604	1.46
AS	5	324	6.83
CRUS	5	442	0.97
USS	5	280	2.66
SGS	5	498	8

cobalt nitrate hexahydrate is dissolved in dry THF, then TMOS and water were added and the homogeneous sol was transferred in a vessel suitable for the evaporation of the solvent and the gelation. The obtained gel was then dried in vacuo at room temperature and finally reduced in flowing hydrogen at 350°C for 12 h (13).

All the samples contained 5 wt.-% Co as confirmed by ICP-AES measurements (Table 1).

Catalyst Characterization

BET - The N_2 (99.9995% purity) adsorption isotherms were obtained using a Sorptomatic 1900 apparatus (Fisons Instruments), by a static volumetric technique. The analysis was controlled by microcomputer processing using MILES-200 and MILEADP software for computations.

H_2 - Chemisorption - Metal dispersions (D_{M}) were measured by single-introduction-back sorption coupled

methods on the basis of irreversibly adsorbed hydrogen, as described elsewhere (14, 15). The samples were pre-treated at 350°C for 4 h in flowing H_2 (30 ml/min), outgassed at the same temperature for 16 h. H_2 uptake was performed at 125°C.

TPR - The experiments were performed using a TPR/O (Thermo Quest Italia). The samples were initially dried under nitrogen at 120°C for 1 h. After cooling to room temperature, a reducing gas mixture (10 vol.-% H_2/N_2) was introduced at a flow rate of 30 ml/min. The temperature was increased to 700°C at a rate of 10°C/min. The H_2 consumption was detected by a TCD (Thermal Conductivity Detector) and recorded as function of temperature.

Catalytic Test

Reaction tests were performed in a stainless steel tubular reactor, inside coated with copper, especially designed for Fischer-Tropsch synthesis of hydrocarbons (C_n : $n < 15$), described elsewhere (16). The reaction was carried out with a mixture of high purity CO and H_2 (SIAD); the H_2/CO ratio of the inlet mixture was 2. The catalysts (always 1 g of fresh sample for each run) were tested four days long at 548 K, 500 kPa and a space velocity (S.V.) of 9.0×10^2 mmolCO/(mmolCo.s); hydrocarbons products were analyzed on-line by gas-chromatography (16).

Table 2.
Activities and Selectivities of Catalysts

Sample	mean CO conversion ^a (%)	C_{H_2} (%)	C_{C_1} (%)	$\text{C}_{\text{C}_2}/\text{C}_{\text{C}_1}$ (%)	$\text{C}_{\text{C}_3}/\text{C}_{\text{C}_1}$ (%)	TOF ($\times 10^3$)
CS	58	52	40	3.8	0.12	5.5
AS	84	40	38	2.2	0.19	8.8
CRUS	54	89	9	0.5	1.12	5.6
USS	87	31	61	0.2	5.04	1.8
SGS	6	0	0	0	0	—
SGS an ^a	0	0	0	0	0	—

^a mean value on 4 days

^b sample pre-activated in air at 300°C for 1 night

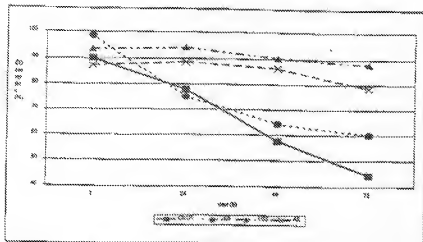


Figure 1. CO conversion vs. time.

Since CO is the only detectable reagent, the mass balance calculation is based on carbon, presuming that the amount entering the reactor is equal to the amount exiting. Therefore, conversion is easily calculated by considering the total number of CO unreacted moles by the number of moles of carbon-containing species found at the exit.

RESULTS AND DISCUSSION

Data on metal dispersion and surface area are summarized in Table 1. It is possible to observe a large difference in DM data changing the catalysts preparation method.

Moreover a drastic change of the BET surface area of the support is reported when the samples are treated with US.

CO conversion (a mean value on four working days), selectivities and turnover frequency (TOF) for all catalyst samples are reported in Table 2. TOFs were calculated using estimated site concentration provided by hydrogen chemisorption measurements ($\text{TOF} = (\text{S.V.} \times \text{CO conversion}) / \text{DM}$).

No activity was shown by SGS as already reported by Okabe et al. (17). In such a catalyst most of the Co particles might be occluded in the SiO_2 matrix and the activation was very difficult. The negligible amount of chemisorbed H_2 on the catalyst corresponded to its low activity.

A pre-activation of the sample in air for one night at 573 K did not give any positive results (see Table 2).

These results are also in agreement with the TPR analysis which shows no hydrogen consumption and thus no reduction of the cobalt sites (Figure 2).

The best catalytic performance is shown by USS (sample prepared using US during the impregnation) with both the best CO conversion and the lowest CH_4 production. This sample also shows the lowest decrease of CO conversion vs. time (Figure 1). On the contrary both CRUS and CS deactivate rapidly with a loss in the conversion > 35% in only four working days.

The catalytic behavior of all the samples are well in agreement with TPR measurements (Figure 2): USS sample shows the highest amount of hydrogen consumption in the lowest temperature range which means a good CO reducibility at a low temperature coupled with a high metal dispersion (Table 1).

CONCLUSIONS

Interesting differences, whether as CO conversion, or selectivity or even deactivation, were obtained in the catalytic performance of Co/ SiO_2 samples changing the preparation methods.

The sample prepared using ultrasound during the first step of the preparation (USS) seems to be the best catalyst showing the highest CO conversion coupled with the lowest C_1 production and a good stability. It is interesting to observe that this catalyst shows the lowest TOF, but the highest DM coupled with the lowest BET surface area in comparison to all the other samples (Table 1 and 2).

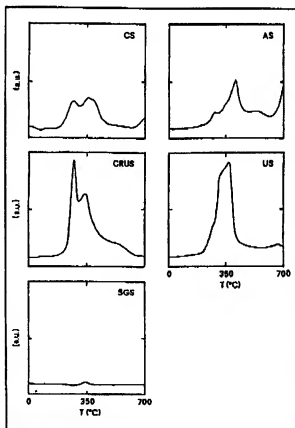


Figure 2. TPR measurements.

LITERATURE CITED

- (1) Schultz, H., *Appl. Catal. A General*, **186**, 3 (1999).
- (2) Reuel, R. C., Bartolomew, C. H., *J. Catal.*, **85**, 78 (1984).
- (3) Iglesia, E., Soled, S. L., Piato, R. A., *J. Catal.*, **137**, 212 (1992).
- (4) Lapszevicz, A., Loeh, H. J., Chipperfield, J. R., *J. Chem. Soc. Chem. Commun.*, 913 (1993).
- (5) Niemela, M. K., Krause, A. O. I., Vaara, T., Lahtinen, J., *Topics in Catalysis*, **2**, 45 (1995).
- (6) Hench, I. L., West, J. K., *Chem. Res.*, **90**, 33 (1990).
- (7) Vansant, E. F., Van der Voort, P., Vrancken, K. C., Characterization and chemical modification of silica surface in: *Studies in surface Science and Catalysis*, **23**, chaps. I and III, Elsevier, Amsterdam, 1995.
- (8) Ro, J. C., Chung, I. J., *J. Non-Cryst. Solids*, **130**, 8 (1991).
- (9) Buckley, A. M., Greenblatt, M., *J. Non-Cryst. Solids*, **143**, 1 (1992).
- (10) Barbier A., Hanif, A., Dailmon, J.-A., Martin, G. A., *Appl. Catal. A*, **168**, 333 (1998).
- (11) Bianchi, C. L., Carli, R., Lanzani, S., Lorenzetti, D., Vergani, V., Ragaini, V., *Ultrasonics - Sonochemistry*, **1**(1), S47 (1994).
- (12) Bianchi, C. L., Carli, R., Fontaneto, C., Ragaini, V., Poncelet, J. Martens, B. Delmon, P. A. Jacobs, P. Grange (eds.), Elsevier, Amsterdam, **21**, 1085 (1995).
- (13) Moggi, P., Predieri, G., Di Silvestri, F., Ferretti, A., *Appl. Catal. A: General*, **183**, 257 (1999).
- (14) Ragaini, V., Giannantonio, R., Magni, P., Lucarelli, L., Leofanti, G., *J. Catal.*, **146**, 123 (1994).
- (15) Giannantonio, R., Ragaini, V. and Magni, P., *J. Catal.*, **146**, 103, (1994).
- (16) Ragaini, V., Carli, R., Bianchi, C. L., Lorenzetti, D., Vergani, G., *Appl. Catal.*, **139**, 17 (1996).
- (17) Okabe, K., Xiaohong, L., Matsuzaki, T., Arakawa, H., Preprints Symposium on Syngas conversion to fuels and chemicals, 21st National Meeting ACS, Anaheim, p. 93 (March 1999).